

THE PHOTOCHEMICAL DECOMPOSITION OF 1,3,5,7-
TETRANITRO-1,3,5,7-TETRAZACYCLOOCTANE (HMX)

Jerry Bert Torbit

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THESIS

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by

Jerry Bert Torbit

April 1970

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The Photochemical Decomposition
of
1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane (HMX)

by

Jerry Bert Torbit
Lieutenant Commander, United States Navy
B. S., United States Naval Academy, 1962

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ABSTRACT

This investigation was concerned with the photochemical decomposition of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX). Products from ultraviolet irradiation on both solid-state HMX and HMX-acetone solutions were obtained and identified.

On the basis of observed product variability with irradiation environment a new mechanism for the photochemical decomposition of HMX was postulated.

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I. INTRODUCTION

Investigations concerning the reaction of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) when subjected to ultraviolet irradiation were first conducted in 1967. Other investigations have been concerned with the thermal decomposition and the effects of nuclear radiation upon HMX. The results of these investigations have been for the most part qualitative in nature, with no general agreement concerning either the reaction products or mechanism having been attained.

The purpose of the present investigation was to attempt to determine the reaction products resulting from ultra-violet irradiation of HMX and thereby to propose a mechanism for the reaction. To accomplish this HMX was irradiated both in the solid state and in acetone solution.

The variation of products with variations of irradiation environment led to the proposal of a new mechanism for photochemical decomposition of HMX.

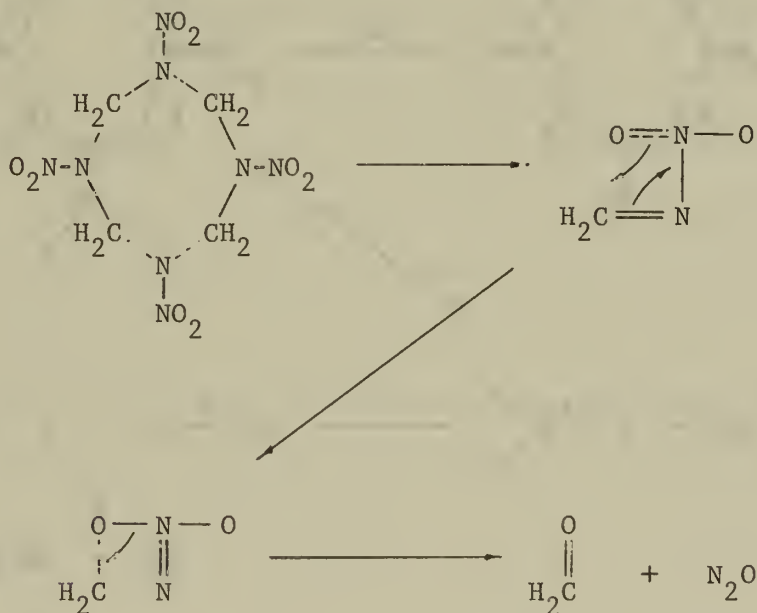
II. HISTORICAL

The explosive compound 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) was first isolated and identified in 1941 by Bachmann and Sheehan [1]. It was encountered as a by-product in the preparation of cyclo-trimethylenetrinitramine (RDX). At that time HMX was considered simply as an impurity in RDX, therefore scant attention was given it. They noted that the new compound was less soluble than RDX in hot aqueous nitric acid and that its melting point was higher than that of RDX, being somewhere above 256° C.

Subsequent crystallographic investigation [2] determined that HMX exists in four polymorphic forms, designated HMX I, HMX II, HMX III and HMX IV. HMX I was found to be the most stable polymorph at room temperature, the other polymorphs being stable at higher temperatures. The initial crystallographic work was refined in later years [3-5] by the use of x-ray diffraction techniques. Only one melting point was found (280° C) for all polymorphs, but solid-state transitions were observed at lower temperatures [5].

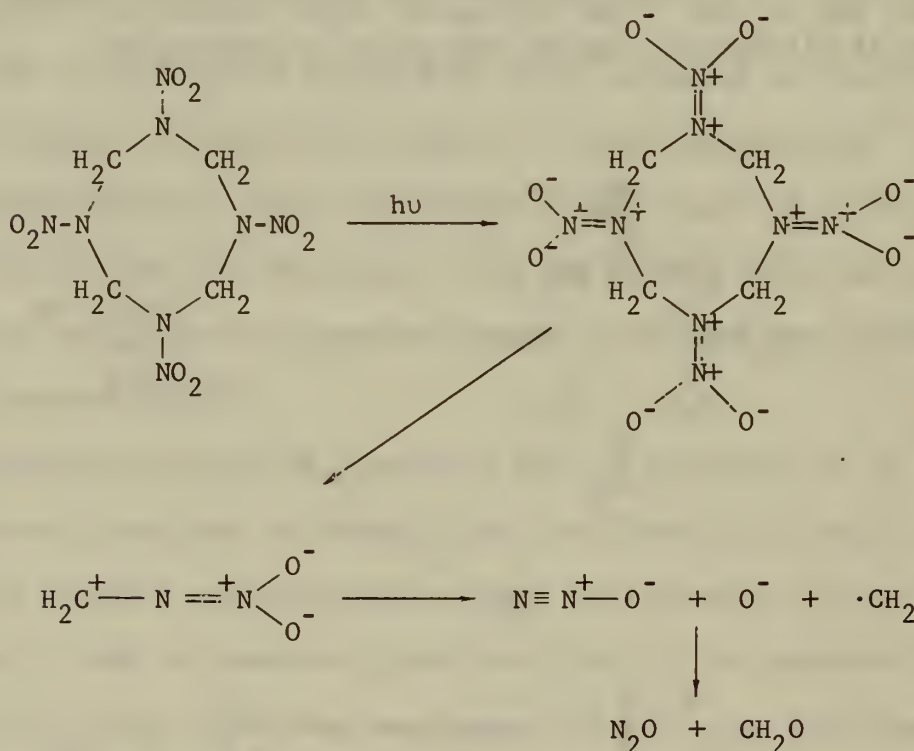
As knowledge accumulated concerning HMX its properties as an explosive were recognized as being in many ways superior to RDX. This realization prompted the generation of many new techniques for the manufacture of HMX in commercial quantities [6-15]. The chemistry of HMX was investigated during the same period [16,17] along with investigations into its absorption characteristics in the infrared [18] and the ultraviolet [19,20] spectra.

As with all explosives, considerations of gross stability or "shelf life" are important. Initial investigation into the thermal stability of HMX by Robertson [21] showed that upon heating above the melting point of 280°C HMX decomposed to give the following gaseous products, quantities given as moles product per mole HMX: NO (0.95), N_2O (1.51), N_2 (1.16), CO (0.57) and CO_2 (0.64). Thermal decomposition studies by Maksinov [22], on the other hand, indicated that the major products were NO and CH_2O . The most recent work on thermal decomposition was conducted in 1967 [23]. This investigation determined the decomposition products to be as follows, quantities given as percentage total product: N_2O (40), NO (9.9), N_2 (9.6), HCN (4.5), CH_2O (8.5), CO_2 (8.5) and CO (4.1). A proposed mechanism for decomposition, obtained through the use of nitrogen-15 tracers, was given as shown below:



Also in 1967, the first report appeared in the literature dealing with effects of ultraviolet irradiation upon HMX [24]. The investigators reported no products, but noted that irradiation caused the solid-state transitions to occur at reduced temperatures.

The most recent investigation into ultraviolet irradiation decomposition of HMX appeared in the literature during the course of this investigation [25]. The major products from ultraviolet irradiation of HMX I were reported to be N_2O and CH_2O . The following mechanism for decomposition was suggested:



Other investigators have studied the effects of nuclear radiation upon the N-NO_2 chromophore [26,27]. Mollay and Prask [28] have investigated the effects of fission-fragment irradiation upon HMX. They concluded that the thermal initiation theory is inadequate to interpret the results of fission-fragment irradiation at elevated temperatures.

III. EXPERIMENTAL

A. PRELIMINARY INVESTIGATION

The first phase of the investigation was to determine if HMX did, in fact, undergo a reaction when subjected to ultraviolet irradiation. To ascertain the presence or absence of photochemical reaction a colorless solution of 0.25 grams of HMX dissolved in 25 cc. of reagent grade acetone was placed in a fused silica reaction vessel and irradiated with a low pressure mercury vapor lamp for a period of four days. Upon completion of irradiation the solution has acquired a pale yellow color. After removing the acetone by means of a rotary evaporator operated at water-aspirator pressure, a light yellow solid remained indicating the possibility that a reaction had taken place. A strong, unidentified odor associated with the light yellow solid product was noted.

At this point the low pressure mercury vapor lamp was replaced with a PEK Labs 200 watt high-pressure mercury short-arc lamp. Another HMX-acetone solution was prepared as above and irradiated for 60 minutes. The results obtained previously were again observed. Pure reagent grade acetone was irradiated for 60 minutes. It remained clear throughout the irradiation. Sixty minute irradiations were conducted using ethyl acetate, cyclohexanone, cyclopentanone and gamma-butyrolactone as solvents. In each case the same color change and product odor was noted. It was further noted that when the solid product from the HMX-acetone solution irradiation was placed in an oven at 70⁰ C for two hours the yellow color appeared to be enhanced, whereas non-irradiated HMX was not visibly affected under the same circumstances. Further irradiations

of HMX-acetone solutions demonstrated that as irradiation time increased the product progressed from a light yellow solid to darker yellow solid to a yellow-brown resinous substance.

On the basis of the results of the preliminary experiments it was considered probable that the HMX had undergone some sort of reaction. Since acetone boils at 56.2°C [29] it was considered unlikely that the reaction could be attributed solely to thermal effects.

The darkening of the yellow color of the solid product upon oven heating at 70°C indicated the possibility that there might have occurred an initial light-induced reaction which produced products more susceptible to thermal degradation than the non-irradiated HMX. To investigate this possibility a solution of 0.5 grams of HMX dissolved in 50 cc. of reagent grade acetone was placed in a pyrex flask connected to a water-cooled condenser and refluxed in a water bath while subjected to natural and fluorescent light. After a period of four hours the solution had acquired a pale yellow color. A fresh solution was prepared and refluxed as above, but in the absence of light. After a period of four hours the solution was found to have remained colorless. Removal of the acetone yielded a white solid identical in appearance to un-treated HMX.

In view of the paucity of information in the literature concerning this problem and the possible ramifications of such a reaction, it was considered worthwhile to explore the photochemistry of the HMX molecule. Determination of quantum yields, construction of energy manifolds and collection of rate data were recognized as being desirable, but due to the limited time available in which to conduct this investigation it

was decided to identify the products of the photochemical reaction and attempt thereby to formulate a possible mechanism for reaction.

B. EQUIPMENT UTILIZED

1. Sample Preparation

All irradiations were conducted using a PEK Labs 200 watt high-pressure mercury short-arc lamp fitted with a parabolic reflector having an image distance of approximately eleven inches. Power was supplied to the lamp using a Oriel universal lamp power supply model number C-72-20. The spectral energy distribution of the lamp may be found on page 16 of PEK Labs catalog 21. The bands with energy in excess of 50 milliwatts per steradian-nanometer are located at 235-250, 305, 313, 330, 365, 405, 435, 545 and 575 nanometers.

Samples were irradiated in cylindrical fused silica reaction vessels permitting a path length of about 2 cm. through flattened irradiation surfaces having areas of about 12 cm². One such vessel was attached to a water-cooled condenser and left open to the atmosphere. Another was fitted to allow connection to a vacuum manifold. A stopcock was located below the manifold connection to allow isolation of the reaction vessel. The reaction vessel was fitted with a side-arm containing a 10/30 standard taper connection to allow sample introduction without breaking the manifold vacuum. The side-arm also served as a connection for gas collection vessels, compressed gas tanks and a thermocouple gauge.

The vacuum system employed allowed collection of three gas samples from each irradiation. Temperature differentiation was attained by cooling the reaction vessel to the desired temperature and sampling the gases remaining uncondensed in the system. Vacuum

was obtained with the use of a single stage oil diffusion pump and with a mechanical vacuum pump connected so that it could also be used as a fore pump. Pressure measurements were made using a mercury manometer and a thermocouple gauge.

Gas samples for infrared absorption analysis were collected in a gas cell with KBr windows. The gas cell provided a path length of nine cm. and contained a volume of 113 cm³. Samples for mass spectrometric analysis were collected in pyrex bulbs attached through a capillary and stopcock to the vacuum manifold. Samples were removed by closing the stopcock and cutting the bulb from the system with a torch.

2. Sample Analysis

The following instruments were used for sample analysis:

Ultraviolet absorption	Beckman DB
Infrared absorption	Perkin-Elmer 621
Nuclear magnetic resonance	Hitachi Perkin-Elmer R-20A
Mass spectroscopy	CEC model A112

C. THIN-LAYER CHROMATOGRAPHIC INVESTIGATION

Samples were prepared by irradiating solutions of 0.15 grams of HMX dissolved in 10 cc. of reagent grade acetone. Irradiations were conducted for various periods of time with the reaction vessel open to the atmosphere through a water-cooled condenser.

A series of 20 by 20 cm. glass plates were covered with a uniform 0.25 mm. layer of aluminum oxide and activated for 30 minutes at 105° C. Samples of non-irradiated and irradiated solutions were spotted on the plates and developed using a solution of 10% diethyl formamide in dichloroethane. Zinc dust and Griess' reagent were used as the indicator [30,31].

Preliminary investigations with various concentrations of non-irradiated HMX dissolved in reagent grade acetone showed that the amount of tailing afforded a visual means of determining the relative concentrations of nitramines present in the samples.

HMX-acetone solutions were prepared as above and irradiated for periods of 30, 60, 90 and 120 minutes. Several thin-layer chromatograms were prepared and analyzed with consistent results.

D. ULTRAVIOLET ABSORPTION INVESTIGATION

Samples were prepared by irradiating 25 cc. portions of a solution of 0.5 grams of HMX dissolved in 100 cc. of reagent grade acetone. Upon completion of irradiation the acetone was removed by means of a rotary evaporator. Since acetone does not transmit ultraviolet light of wavelengths shorter than 330 $m\mu$ [32] it was necessary to find a solvent transparent in the ultraviolet region of the spectrum. The major criteria for a solvent were considered to be the ability to dissolve HMX, adequate transmission of light of wavelengths greater than 210 $m\mu$ and absence of interfering reactions with either the non-irradiated HMX or the irradiation products. Acetonitrile, cyclohexane, heptane and hexane all transmit wavelengths in the ultraviolet region greater than 210 $m\mu$ [32]. Of these solvents, acetonitrile was experimentally determined to be the most satisfactory. As a result, spectrograde acetonitrile was used as the solvent in all ultraviolet absorption investigations.

Preliminary measurements showed that only one absorption peak at 227 $m\mu$ was present for both the non-irradiated and the irradiated HMX. The strength of this peak decreased with increased time of irradiation. By a trial and error method it was determined that to obtain the best

ultraviolet absorption spectrum the optimum concentration of HMX ([HMX]) in acetonitrile was 4×10^{-5} moles/liter (M). A solution of 0.5 grams of HMX dissolved in 100 cc. of reagent grade acetone was prepared. Ten cc. aliquots of this solution were taken for individual irradiation and analysis. One aliquot was not irradiated, while others were irradiated for periods of 10, 20, 30, 40 and 50 minutes. Upon completion of irradiation the acetone was removed by means of a rotary evaporator. Of each remaining solid 0.0030 grams were dissolved in sufficient acetonitrile to give 10 cc. of solution. One cc. of each such solution was then diluted with pure acetonitrile to 25 cc. This procedure resulted in the non-irradiated sample having an [HMX] of 4×10^{-5} M, the irradiated samples differing from this depending upon the amount of reaction having taken place.

E. INFRARED ABSORPTION INVESTIGATIONS

Samples for infrared absorption analysis were prepared by irradiating HMX both as a solid and as an HMX-acetone solution. Both solid and gaseous products were collected and analyzed.

1. Preparation of Solid Products

Solid products were obtained by irradiating a solution of 0.5 grams of HMX dissolved in 25 cc. of reagent grade acetone in a fused silica reaction vessel open to the atmosphere. Solutions were irradiated for periods of time varying from fifteen seconds to four hours. Upon completion of irradiation the acetone was removed by means of a rotary evaporator. A portion of the remaining solid was mixed with sufficient KBr to yield a pellet approximately 0.5 mm. thick. Preparation and analysis was carried out for 26 such samples, including non-irradiated HMX and RDX. An additional infrared absorption spectrum

was obtained from a KBr pellet prepared using the solid product isolated as described in section III F.

2. Collection of Gaseous Products

a. Irradiation of Solid HMX

HMX irradiations in the solid state were carried out in a fused silica reaction vessel attached to a vacuum manifold. 0.5 and 0.1 gram samples of HMX were deposited from a supersaturated acetone solution upon the inner surface of the reaction vessel. Deposition was carried out so as to place a thin even coating of HMX upon one flattened surface of the reaction vessel, the other surface remaining clean. The reaction vessel was placed on the vacuum line, evacuated to about 10^{-3} Torr and allowed to de-gas for three days. The reaction vessel was positioned so that the light beam passed through the clean vessel surface before striking the HMX deposited on the opposite surface. Irradiations were then carried out with a stream of cool air directed over the reaction vessel, thus maintaining the HMX at or near room temperature in order to avoid thermal decomposition due to heating from the lamp. This procedure was employed for both the 0.5 and the 0.1 gram samples. It was found that satisfactory gas samples could be obtained by irradiating the 0.1 gram samples for 90 minutes. Samples for infrared analysis were taken at 20 and -78.5° C. An additional irradiation of approximately 0.2 grams of solid-state HMX was carried out under an atmosphere of helium at a pressure of 20 cm. of mercury. A sample for infrared analysis was taken at 20° C.

b. Irradiation of HMX-Acetone Solutions

A solution of 0.5 grams of HMX dissolved in 25 cc. of acetone was prepared and placed in the reaction vessel attached to the

vacuum manifold. The solution was cooled to -78.5°C and the system was evacuated to 10^{-3} Torr. The reaction vessel was then isolated from the manifold and irradiated for three hours. Upon completion of irradiation the sample solution was cooled to the desired temperature and the product gases allowed to expand into the system. Samples were taken at 20, -3, -78.5 and -195.8°C .

F. NUCLEAR MAGNETIC RESONANCE INVESTIGATION

Samples were prepared by dissolving 0.5 grams of HMX in 100 cc. of reagent grade acetone and irradiating 25 cc. portions of the solution for four hours. It was found that whereas HMX is insoluble in non-organic solvents the yellow-brown product was readily soluble in H_2O . Separation of products from remaining non-reacted HMX was accomplished by placing the residue in H_2O and filtering to remove the HMX. The H_2O was then removed by vacuum distillation and the resulting brown solid was weighed. Product solutions of approximately 15% by weight were prepared using D_2O as the solvent. The D_2O used contained one percent DDS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) which provided a reference at 0 ppm. [33].

G. MASS SPECTROSCOPIC INVESTIGATION

The procedures used to produce gas samples for mass spectroscopic analysis were identical to those used to produce gas samples for infrared absorption analysis. Product gases were allowed to expand into pyrex bulbs of 20 cc. capacity and removed by cutting the bulbs from the vacuum manifold with a torch. Samples were collected at temperatures of 20, -78.5 and -195.8°C from solid state HMX and HMX-acetone solution irradiations. One sample was collected from the

solid-state irradiation of HMX under an atmosphere of helium at a pressure of 20 cm. of mercury. Mass to charge (m/e) ratios from 12 to 110 were investigated.

H. PHYSICAL PARAMETERS

1. Mass Loss and Gas Evolution Measurements

To obtain a measure of the mass loss of HMX upon irradiation a fused silica reaction vessel was first carefully cleaned and weighed. A sample of HMX weighing approximately 0.3 grams was then deposited from a supersaturated HMX-acetone solution upon one inside surface of the reaction vessel. After completely removing the acetone by oven drying for thirty minutes at 70° C the reaction vessel was again weighed, thus determining the precise mass of HMX deposited on the reaction surface to be 0.2784 grams. The sample was then irradiated while exposed to the atmosphere for two successive 90 minute periods. At the end of each irradiation period the vessel was weighed and the mass loss calculated.

To determine the relation between the mass lost and the quantity of gas evolved a 0.5036 gram sample of HMX was deposited on the inside surface of the reaction vessel fitted for connection to the vacuum manifold. The reaction vessel was placed on the vacuum manifold and the system was evacuated to 10^{-3} Torr and allowed to de-gas for three days. The sample was then irradiated for 18 hours, the reaction vessel being cooled throughout this period by a stream of cool air. Throughout the period of irradiation the evolved gases were allowed to expand into the vacuum manifold, the volume of which had been previously determined. Upon completion of irradiation the pressure of the evolved gases was recorded.

The reaction vessel was removed from the manifold and the remaining solid was quantitatively transferred to a previously weighed flask by repeated washings with reagent grade acetone. The acetone was removed by means of a rotary evaporator and the flask was again weighed.

2. Melting Point Determinations

Melting points were obtained with a Fisher-Johns melting point apparatus and are presented herein as uncorrected values.

The melting point determined for non-irradiated HMX was within two degrees of a published value [5]. The melting point values obtained for irradiated samples varied widely, decreasing with increasing period of irradiation. The melting point of the pure product separated by H_2O solution and filtering was determined with good consistency.

3. Effects of Irradiation Upon Impact Sensitivity

A sample of irradiated HMX was prepared by dissolving 0.7 grams of HMX in 50 cc. of reagent grade acetone and irradiating the solution for 30 minutes in a fused silica reaction vessel open to the atmosphere. Upon completion of irradiation the acetone was removed by means of a rotary evaporator leaving a yellow solid.

Impact sensitivity determinations were conducted on both non-irradiated and irradiated HMX using the drop-test technique as outlined in Ref. 34. This method determines relative impact sensitivities of compounds on the basis of drop heights required for a given mass to attain a 50% probability of detonation upon impact with a static sample.

IV. RESULTS

Thin-layer chromatograms afforded visual evidence of a decreasing nitramine concentration with increasing period of irradiation. There was no indication of nitramines other than HMX present in the product.

The single absorption peak observed in the ultraviolet spectrum at 227 m μ was determined to be due to the N-NO₂ chromophore [19,20,35,36]. The decreasing strength of this band with increasing irradiation time showed the [N-NO₂] to be a function of the period of irradiation.

Beer's law [32] was assumed to be valid in this instance and was accordingly used to calculate the absorptivity of the N-NO₂ chromophore from the known concentration of the non-irradiated sample. The value for absorptivity thus obtained was used to calculate the [N-NO₂] for each of the irradiated samples. The results of those calculations are presented in Figure 1. The linear relationship shown in Figure 1 would indicate the presence of zero-order kinetics.

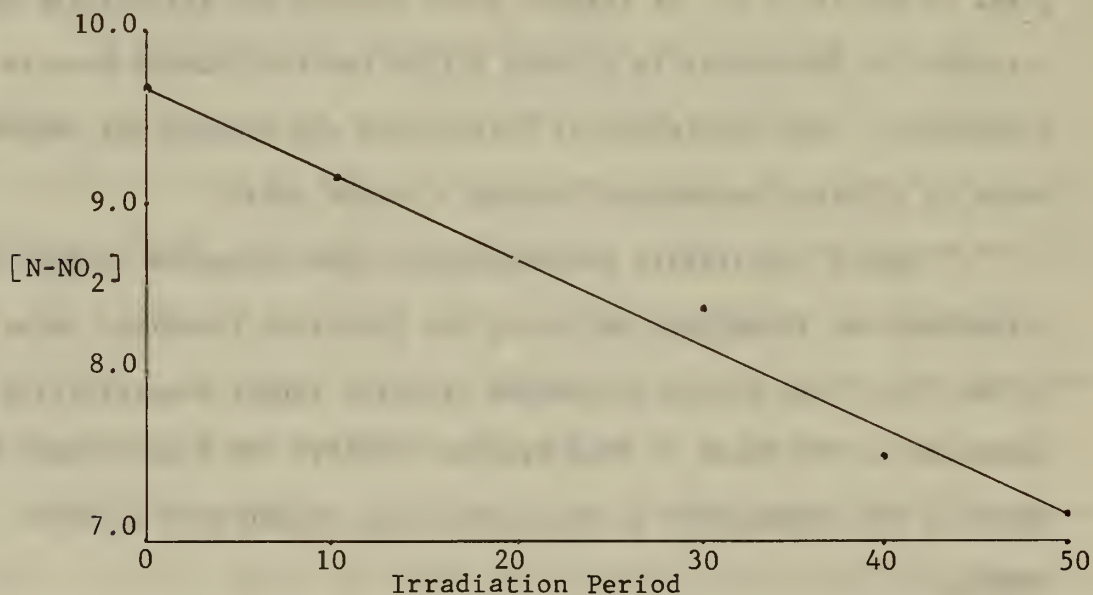


Figure 1. [N-NO₂] (g/l × 10³) plotted as a function of irradiation period (minutes).

The HMX used in this investigation was ascertained to be in the form of the polymorph HMX I by comparison of infrared spectra obtained from non-irradiated HMX and published spectra for the polymorphs HMX I, HMX II and HMX III [5].

The only indication of change in molecular structure evidenced by the spectra of the solid products from irradiation of HMX-acetone solution was a marked decrease in the intensity of major absorption peaks at wave numbers 1275 and 1560. By the use of correlation charts provided by Beckman Instrument Corporation and Refs. 32 and 33 these peaks were identified as, respectively, single-bond and double-bond vibrations in the N-NO₂ chromophore. The intensity of these peaks continued to decrease with increased periods of irradiation.

The infrared absorption spectrum of the isolated, water-soluble solid product showed broad, ill-defined bands around wavenumbers 1380 and 1670 and a very broad absorption in the area of wavenumber 3400.

The gaseous products obtained at 20° C from HMX-acetone solution irradiation yielded a spectrum showing strong (s), medium (m) and weak (w) absorption bands at wavenumbers 270 (s), 520 (m), 580 (m), 660 (w), 770 (w), 900 (w), 1080 (w), 1210 (s), 1270 (m), 1300 (s), 1360 (s), 1430 (w), 1730 (s), 2130 (w), 2210 (s), 2230 (s), 2330 (m), 2550 (w), 2800 (w), 2970 (m), 3020 (m), 3460 (m) and 3490 (m).

Comparison of this spectrum with that obtained from reagent grade acetone vapor showed the bands at wavenumbers 580 (m), 660 (w), 1270 (m), 1300 (s), 1430 (w), 2210 (s), 2230 (s), 2350 (w), 2560 (w), 2800 (w), 3020 (m) and 3490 (m) to be attributable to irradiation products.

Decreasing the temperature at which the product gases were collected resulted in reduction of band intensities as shown in Table 1. Dashes indicate the absence of the band. T_c represents the temperature in degrees centigrade at which the product gases were collected.

T_c	WAVENUMBER					
	580	660	1270	1300	1430	2210
20.0	m	w	m	s	w	s
-3.0	m	-	-	m	w	m
-78.5	w	-	-	m	-	w
-195.8	w	-	-	w	-	-

T_c	WAVENUMBER					
	2230	2350	2560	2800	3020	3490
20.0	s	w	w	w	m	m
-3.0	m	-	-	-	w	-
-78.5	w	-	-	-	-	-
-195.8	-	-	-	-	-	-

Table 1. Infrared absorption bands for gaseous products obtained from ultraviolet irradiation of a solution of HMX dissolved in acetone.

The gaseous products obtained at 20° C from an 18 hour irradiation of HMX in the solid state yielded a spectrum showing absorption bands at wavenumbers 270 (s), 580 (m), 660 (m), 820 (s), 1280 (m), 1430 (s), 1760 (m), 2210 (m), 2230 (m) and 2350 (m). The spectrum obtained from the sample collected at -78.5° C showed that the intensity of the bands at wavenumbers 580, 2210, 2230 and 2350 had been reduced and the bands at wavenumbers 660 and 1280 had been altogether eliminated.

The infrared spectrum of the gaseous products from the solid-state irradiation of HMX under an atmosphere of helium at a pressure of 20 cm. of mercury differed from those of the solid-state irradiation of

HMX under high vacuum only in that it lacked the bands at wavenumbers 660 and 2350 and that the bands at wavenumbers 2210 and 2230 were of lesser intensity.

The nuclear magnetic resonance spectra obtained gave no evidence of proton presence in the isolated brown solid product.

The results of mass spectroscopic analysis of gaseous samples obtained from irradiation of HMX-acetone solutions are summarized in Table 2. Quantities are expressed as percentages relative to major product.

T_c	MASS TO CHARGE RATIO									
	13	14	15	16	26	27	28	29	30	31
20.0	2.0	8.0	34.0	3.5	5.5	9.3	12.7	4.1	0.1	0.5
-78.5	0.5	11.0	3.4	3.0	0.9	1.5	100	1.6	1.9	0.0

T_c	MASS TO CHARGE RATIO								
	32	38	39	40	41	42	43	44	58
20.0	0.1	1.2	3.8	0.9	1.9	7.5	100	4.2	24.0
-78.5	6.7	0.1	0.3	1.7	0.2	0.5	5.8	5.5	3.0

Table 2. Mass to charge ratios of gaseous products obtained from ultraviolet irradiation of a solution of HMX dissolved in acetone.

The results obtained from the irradiation of a solution of HMX dissolved in acetone- d_6 are shown in Table 3. Quantities obtained for each mass-to-charge ratio (m/e) are expressed as percentages relative to major products (%).

m/e	14	16	18	28	30	32	34
%	1.9	2.4	35.5	5.4	8.7	1.6	1.6
m/e	40	42	44	45	46	47	64
%	1.3	1.6	6.3	1.5	100	2.3	30.0

Table 3. Mass to charge ratios of gaseous products obtained from ultraviolet irradiation of a solution of HMX dissolved in acetone- d_6 .

The results obtained from analysis of vapors collected at 20° C from non-irradiated (N) and irradiated (I) reagent grade acetone are shown in Table 4. Quantities are expressed as percentages relative to major product.

m/e	14	15	16	26	27	28	29	30
N	6.8	33.3	0.5	5.5	8.9	1.9	3.8	0.2
I	12.7	57.1	2.8	8.4	13.5	31.9	7.3	3.1

m/e	38	39	40	41	42	43	44	58
N	1.3	4.0	0.8	2.1	7.5	100	2.4	25.0
I	1.2	4.1	1.1	2.2	7.5	100	3.5	25.9

Table 4. Mass to charge ratios of gaseous products obtained from ultraviolet irradiated and non-irradiated reagent grade acetone.

The results from analysis of gaseous products obtained at various temperatures from irradiation of HMX in the solid state are shown in Table 5. Quantities are expressed as percentages relative to the major product.

T _c	MASS TO CHARGE RATIO							
	14	16	28	29	30	32	40	44
20.0	10.9	3.1	100	0.8	0.4	17.6	1.9	1.3
-78.5	10.6	3.2	100	0.8	0.1	18.8	2.0	0.5
-195.8	11.5	3.2	100	0.9	0.0	20.5	2.5	0.4

Table 5. Mass to charge ratios of gaseous products obtained from ultraviolet irradiation of solid-state HMX under a pressure of 0.001 Torr.

The results from analysis of gaseous products obtained at 20° C from irradiation of HMX in the solid state under an atmosphere of helium at a pressure of 20 cm. of mercury are shown in Table 6.

m/e	14	28	30	44
%	17.1	100	67.0	51.5

Table 6. Mass to charge ratios of gaseous products obtained from ultraviolet irradiation of solid-state HMX under an atmosphere of helium at a pressure of 20 cm. of mercury.

The mass loss upon irradiation of the 0.2784 grams of solid HMX exposed to the atmosphere was found to be 0.0006 grams after a period of 90 minutes and 0.0025 grams after a period of 180 minutes.

The mass loss upon irradiation of the 0.5036 gram sample for 18 hours was found to be 0.0567 grams or 1.91×10^{-3} moles. Using the ideal gas law the 65 cm. Hg of gaseous products evolved was found to represent 1.99×10^{-2} moles of gas evolved.

The melting point obtained for HMX was $278 \pm 2^\circ$ C. The melting point obtained for the isolated water-soluble product was $88 \pm 2^\circ$ C.

Analysis of the drop-test data showed that the non-irradiated HMX required a drop height of 35 cm. for 50% probability of detonation, whereas for the sample irradiated for 30 minutes a drop height of 78 cm. was required to obtain the same probability.

V. DISCUSSION

The reduction of nitramine concentration with increased irradiation time as shown by the thin-layer chromatograms indicates that ultraviolet irradiation of an HMX-acetone solution results in destruction of the N-NO₂ chromophore. The lack of evidence for the presence of nitramines other than HMX was not considered sufficient to eliminate this possibility, due to the low [HMX] necessitated by solubility limits [31]. Destruction of the N-NO₂ chromophore is also shown by the ultraviolet and infrared absorption spectra.

Using the correlation charts provided by Beckman Instrument Corporation and Refs. 32, 33, 37, 38 and 39 the major products obtained at 20° C from HMX-acetone solution irradiation (Table 1) were identified. The bands at wavenumbers 660 (w) and 2350 (w) were assigned to CO₂, those at 1300 (s), 2210 (s) and 2230 (s) to N₂O. The band at wavenumber 3020 (m) was attributed to a mixture of CH₂O and C₂H₄. The band expected at wavenumber 1700 for CH₂O was considered to have been masked by a strong acetone band in that region. Since the boiling (sublimation for CO₂) points of the identified products decrease in the order CH₂O, CO₂, C₂H₄ and N₂O [29], the decrease in band intensities with decreasing T_c as noted in Table 1 are in agreement with these assignments.

Using the same references as above, the major gaseous products obtained at 20° C from the solid-state irradiation of HMX were identified. The bands at wavenumbers 660 (m), 2350 (m), 1280 (m), 2210 (m) and 2230 (m) again indicated the presence of CO₂ and N₂O. The band at wavenumber 1430 (s) was attributed to C₂H₆. The decrease in band intensities with decreased T_c was again in agreement with these assignments.

For the sample obtained from irradiation of solid-state HMX under a helium atmosphere the lack of bands at wavenumbers 660 and 2350 indicated that formation of CO_2 was reduced below the limits of detectability. The lack of the CO_2 bands was determined with the use of a consistent product peak as an internal reference.

The infrared spectra obtained from the isolated water-soluble solid product showed no indication of the presence of N-H or C-H bonds. This observation was in agreement with the lack of protons as indicated by the nuclear magnetic resonance spectrum. The broad band around wavenumber 3400 was attributed to H_2O absorbed by the product. The broad, ill-defined bands at wavenumbers 1380 and 1670 were not identified.

As shown in Table 2, the major products obtained at 20°C from irradiation of HMX-acetone solution were those having mass-to-charge ratios of 15, 28, 43 and 58. With the use of Ref. 33 these ratios were assigned as follows: 15 (CH_3^+), 28 (N_2 , C_2H_4), 43 ($\text{O}=\text{C}^+-\text{CH}_3$), 58 (acetone). The reduction of the peaks at ratios 15, 43 and 58 and the emergence of 28 as the major peak at T_c of -78.5°C was consistent with these assignments. The shifts of the peaks at ratios 15, 43 and 58 to ratios 18, 46 and 64 when acetone- d_6 was used as the solvent (Table 4) identified these peaks as being due to the solvent.

Again referring to Table 2 it is seen that upon removal of most of the solvent by collecting the sample at -78.5°C the major peaks occurred at m/e ratios of 14, 28, 32 and 44. These peaks were assigned as follows: 14 (N), 28 (N_2 , C_2H_4), 32 (O_2), 44 (N_2O , CO_2). The

possibility of a portion of the peak at m/e ratio of 28 being due to CO was discounted due to the lack of a CO band at wavenumber 2143 in the associated infrared absorption spectrum.

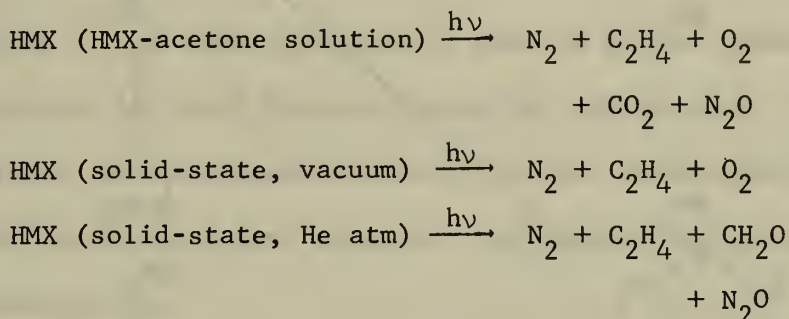
Reference 40 states that the primary products of the unquenched photochemical decomposition of acetone are $\cdot\text{CH}_3$ and CO. Quenching of this reaction by a third body capable of absorbing excess vibrational energy from the acetyl group results in the primary products $\text{O}=\dot{\text{C}}-\text{CH}_3$ and $\cdot\text{CH}_3$.

The large signal obtained at m/e ratio of 28 for the products from irradiation of pure acetone (Table 4) indicates significant formation of CO. The amount of CO obtained from irradiation of HMX-acetone solution (Table 3) is much less than that obtained from irradiation of pure acetone. This fact suggests that the unquenched mechanism for acetone photolysis is not significantly involved in the photochemical reaction of an HMX-acetone solution. The presence of the HMX may therefore account for the reduced generation of CO by quenching the acetone reaction through a third body effect. The energy thus absorbed might serve to activate the HMX, but no definite conclusions in this regard can be made without quantum yield data. The possibility of such an activation, in addition to the possibility of gas-phase reactions of acetone fragments with HMX products, necessitates caution in the interpretation of the results of HMX-acetone photolysis.

The major m/e ratios obtained from solid-state irradiation of HMX (Table 5) were assigned as follows: 14 (N), 16 (O), 28 (N_2 , C_2H_4), 32 (O_2). CO was considered not to be a significant product on the basis of the absence of CO bands in the associated infrared spectrum. The persistence of these peaks at temperatures down to -195.8°C is

consistent with these assignments. The presence of CO_2 and N_2O as noted in the infrared absorption spectrum was detected at m/e ratio of 44, but as shown in Table 5 they were minor products.

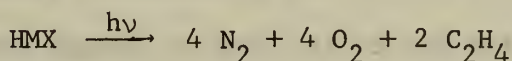
The major products obtained under differing irradiation environments can be summarized as below:



NO was considered not to be a significant product in the latter case due to the absence of NO bands in the associated infrared spectrum.

From the above it can be seen that N_2 and C_2H_4 are present in quantity under all irradiation conditions. The O_2 produced by solid-state irradiation under a vacuum of 10^{-3} Torr is replaced by CH_2O and N_2O when irradiation is carried out under a helium atmosphere of 20 cm. of mercury. The lack of significant amounts of CH_2O , the appearance of CO_2 and the reappearance of O_2 as major products upon irradiation of HMX-acetone solution were not considered to be reliable indications of HMX photolysis products due to the complications noted above.

The values obtained for mass loss and gas evolution upon solid-state irradiation of HMX under vacuum indicated that each mole of HMX reacted yields ten moles of gaseous products. The production of N_2 , O_2 and C_2H_4 is stoichiometrically consistent with this ratio as shown below:



a proposed mechanism accounting for these products is shown as Figure 2.

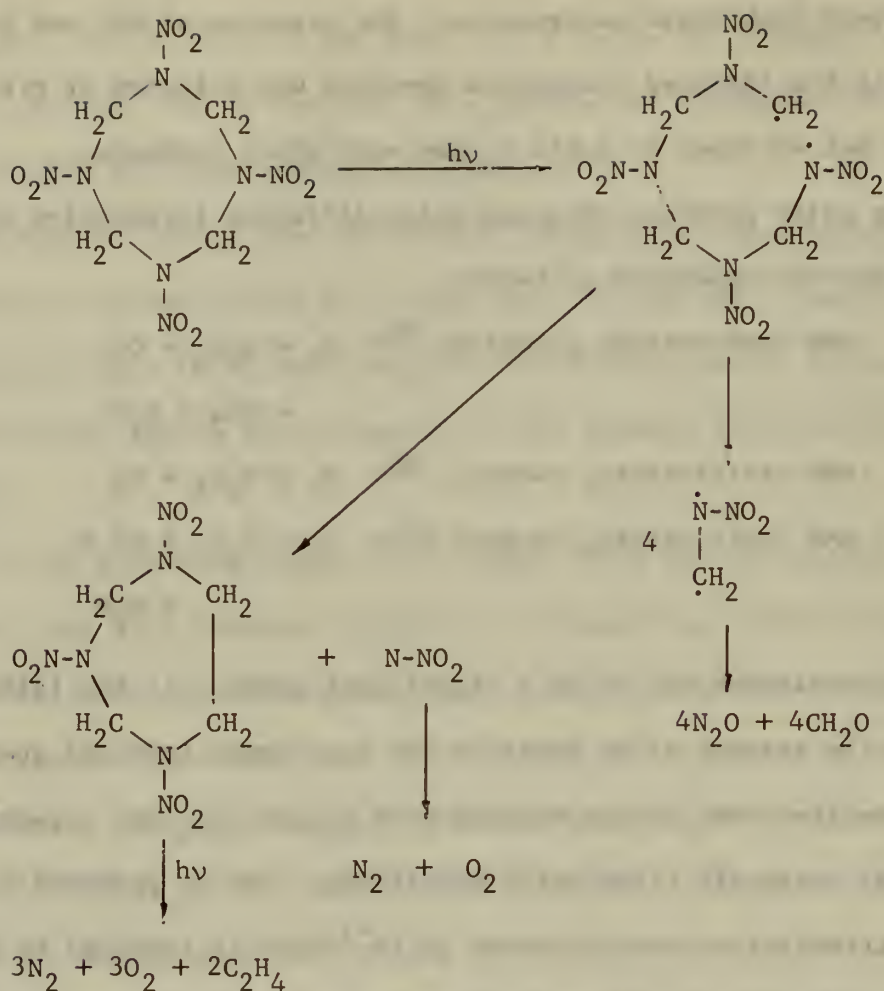


Figure 2. Proposed mechanism for photochemical decomposition of HMX.

The mechanistic pathway leading to the products N_2 , O_2 and C_2H_4 is supported by the data presented in Figure 1, which shows that with increased irradiation period the N-NO_2 in the solid residue decreased. Since each sample analyzed was prepared from the same mass of product, this indicated that some product was formed having fewer N-NO_2 chromophores per gram than the original HMX. The presence of such an intermediate product is also indicated by the reduced shock sensitivity as demonstrated by the drop-test data. The intermediate species would be expected to be less sensitive due to the reduced oxygen balance.

The mechanistic pathway leading to the products N_2O and CH_2O is the same as the mechanism proposed by Maycock, et. al. [25].

The experimental results indicate that the predominant mechanistic pathway will be in some manner determined by the pressure under which the irradiation is conducted. It should also be recognized that the production of N_2O and CH_2O might in part be due to thermal decomposition brought about by local heating within the HMX crystal. More definite conclusions in these regards require further investigation utilizing equipment capable of more effective temperature and pressure control and determination.

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13. ABSTRACT

This investigation was concerned with the photochemical decomposition of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX). Products from ultraviolet irradiation of both solid-state HMX and HMX-acetone solutions were obtained and identified.

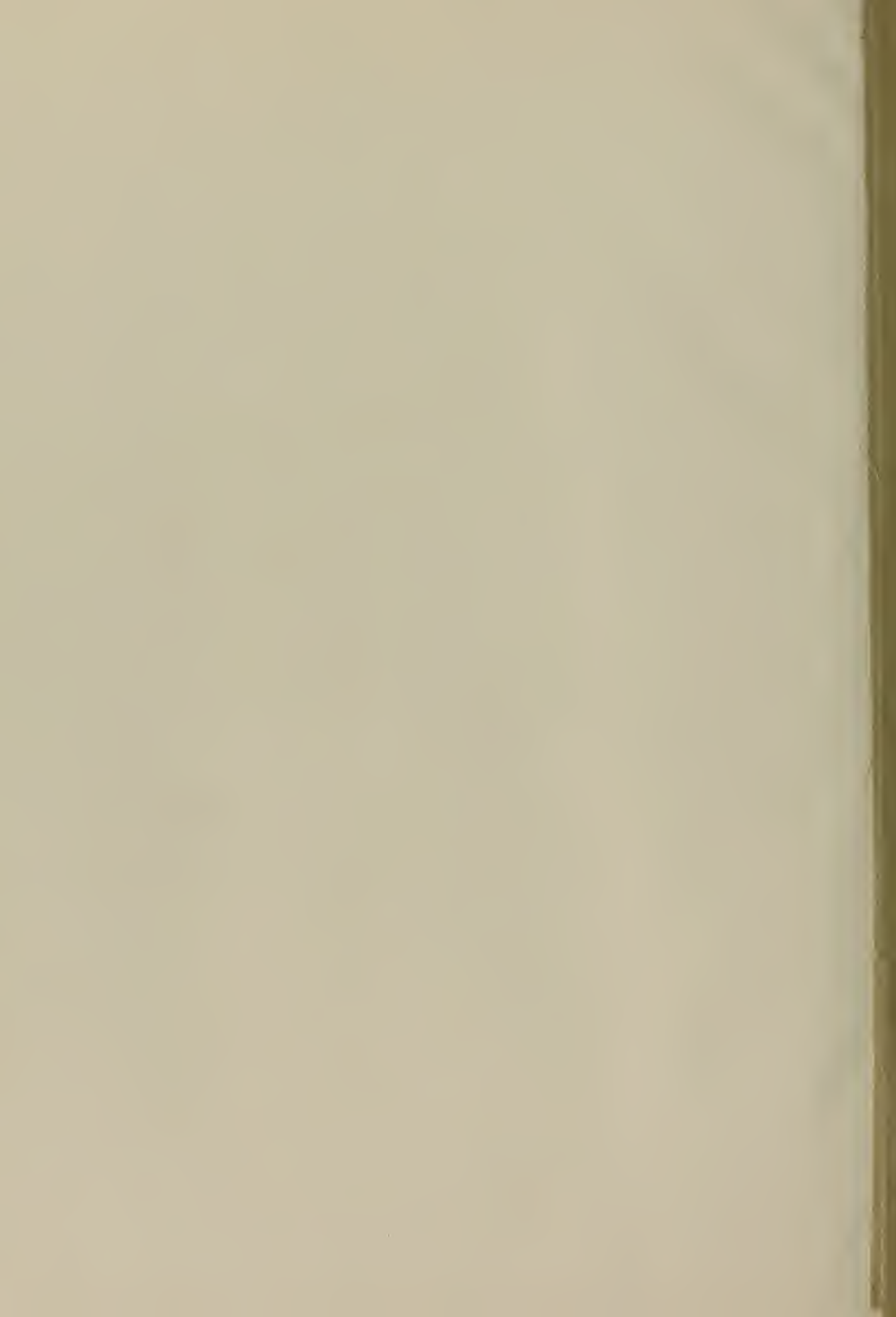
On the basis of observed product variability with irradiation environment a new mechanism for the photochemical decomposition of HMX was postulated.

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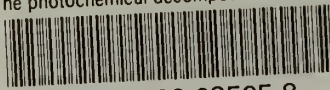
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